



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification<sup>5</sup>:

C01B 21/20

A1

(11) International Publication Number:

WO 94/26659

(43) International Publication Date: 24 November 1994 (24.11.94)

(21) International Application Number:

PCT/US94/05117

(22) International Filing Date:

9 May 1994 (09.05.94)

(30) Priority Data:

08/058,949

7 May 1993 (07.05.93)

US

(71) Applicant: NALCO FUEL TECH [US/US]; 1001 Frontenac Road, Naperville, IL 60563 (US).

(72) Inventors: COMPARATO, Joseph, R.; 10627 South Quail Ridge Court, Naperville, IL 60564 (US). SUN, William, H.; 987 Amberwood Circle, Naperville, IL 60563 (US). MICHELS, William, F.; 1195 Dogwood Lane, Aurora, IL 60564 (US).

(74) Agents: CARVIS, Thaddius, J. et al.; St. Onge Steward Johnston &amp; Reens, 986 Bedford Street, Stamford, CT 06905 (US).

(81) Designated States: AU, CA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

## Published

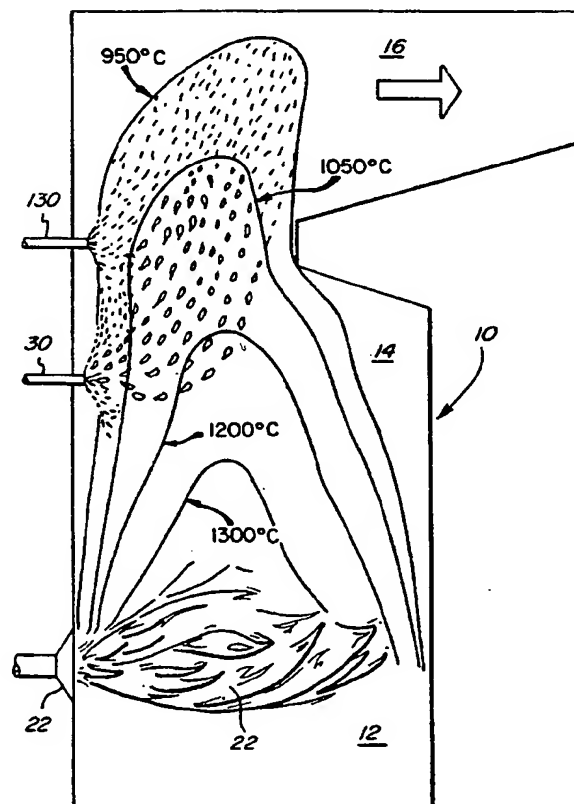
With international search report.

With amended claims and statement.

(54) Title: PROCESS AND APPARATUS FOR ENHANCING DISTRIBUTION OF NO<sub>x</sub>-REDUCING CHEMICALS IN A HIGH-SOLIDS ENVIRONMENT

## (57) Abstract

Reduction of nitrogen oxides emissions from large scale combustors, such as coal-fired boilers and incinerators which produce effluents with high solids concentrations, is improved. High solids loading and other operational factors can cause such large temperature gradients transverse to the direction of effluent flow the SNCR cannot be practiced in conventional fashion. The process entails defining a near-wall zone having a temperature effective for SNCR and a central zone where the temperature is too high. NO<sub>x</sub>-reducing composition is introduced into the effluent within the near-wall zone in fine droplets (30 and 130) and can be introduced into the central zone after the gas has cooled or as large droplets effective to survive the high temperature.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

**PROCESS AND APPARATUS  
FOR ENHANCING DISTRIBUTION OF  
NO<sub>x</sub>-REDUCING CHEMICALS IN  
A HIGH-SOLIDS ENVIRONMENT**

**DESCRIPTION**

**Technical Field**

The invention relates to reducing the environmental damage caused by large-scale combustion, and provides improved processes and apparatus for achieving this, especially in the field of NO<sub>x</sub> reduction by selective noncatalytic reduction (SNCR) in effluents where influences such as high solids contents create large temperature gradients transverse to the direction of flow.

The oxides of nitrogen (NO<sub>x</sub>) contribute to smog, ground level ozone formation, and acid rain. The major sources of anthropogenic NO<sub>x</sub> emissions are stationary and mobile combustion of carbonaceous materials, such as coal, oil and gas, as well as refuse and organic industrial chemicals. These materials are burned at such high temperatures (e.g., 1000° to 1700°C) in large scale combustors, that the

-2-

conditions favor formation of free radicals of oxygen and nitrogen and their chemical combination as nitrogen oxides. Titles 1, 3, and 4 of the Clean Air Act Amendments of 1990 address the control of NO<sub>x</sub> emissions from stationary sources to limit ground level ozone and acid rain.

To reduce the emission of NO<sub>x</sub>, both primary and secondary measures have been employed. Primary measures are those which modify combustion itself and may involve using an excess of air or fuel or a combination of both in staged combustion. However, such measures are typically expensive and present only partial remedies.

A number of economically-attractive secondary measures have been developed which enable combustion under efficient conditions, with resultant NO<sub>x</sub> generation, but then reduce the NO<sub>x</sub> by converting it to other compounds which can either be emitted or eliminated from the flue gas. Of these, selective gas phase reactions -- both catalytic (SCR) and non-catalytic (SNCR) -- are advantageous because they permit NO<sub>x</sub> reduction while using relatively low levels of chemical reducing agents. The SNCR procedures are especially effective and economical for many applications, especially those where particulates could cause fouling of catalysts.

However, the attainment of consistent, high reductions in NO<sub>x</sub> with SNCR procedures is a matter of considerable engineering and chemistry, especially where large temperature gradients occur across a plane where chemical injection is desired, such as in effluents containing high levels of entrained solids. These SNCR reactions occur in the gas phase and typically involve NO<sub>x</sub> levels of 20 to 1500 parts per million by volume (ppm<sub>v</sub>) and either urea or ammonia at from one to three times the amount stoichiometrically required. The reactions require mating of the reactive mate-

-3-

rials in high dilution in the gas phase at the correct temperature.

Typically, the  $\text{NO}_x$ -reducing agents are introduced in aqueous droplets. For best results, the water must be evaporated from the droplets and the active agent converted to the gas phase to achieve contact with the  $\text{NO}_x$  molecules in the temperature range effective for reaction, e.g., from  $850^\circ$  to  $1150^\circ\text{C}$ . In the cases of coal-fired furnaces and those which require the injection of solid adsorbents to control the emission of sulfur oxides ( $\text{SO}_x$ ), it has now been determined that the high levels of solids that become entrained in the effluent gases can create such extreme cross-sectional temperature gradients that SNCR procedures which attempt chemical injection across the entire cross section of an effluent passage, are rendered inefficient and productive of secondary pollutants. Unfortunately, space limitations and combustor geometry often greatly limit injector location to just such circumstances.

High levels of entrained solids affect the dynamics of evaporation of the water from treatment droplets and release of the active chemicals. Results have often been inconsistent when conventional means have been used in high solids environments, even where the desired temperature conditions were apparently being met. Temperature gradients of from  $100^\circ$  to  $350^\circ\text{C}$ , and greater, can be created by the tendency of the solids to attenuate or refract the transmission of radiation from the gas to the heat absorbing surfaces. This can make some areas of a cross section too cold and others too hot. If too cold, the droplets can impact the equipment surfaces and/or form undesirable by-products such as ammonia, and, if too hot, the active chemical can be oxidized to form further  $\text{NO}_x$ .

-4-

There is a need for improved distribution of active SNCR chemicals in combustion effluents which exhibit large cross-sectional temperature gradients, such as those heavily loaded with entrained particulates.

### Background Art

Prominent among the SNCR processes are those disclosed by Lyon in U.S. Patent 3,900,554 and by Arand et al in U.S. Patents 4,208,386 and 4,325,924. Briefly, these patents disclose that ammonia (Lyon) and urea (Arand et al) can be injected into hot combustion gases to selectively react with  $\text{NO}_x$  and reduce it to diatomic nitrogen and water.

The SNCR process described by Lyon reduces the concentration of nitrogen monoxide ( $\text{NO}$ ). Lyon discloses injecting ammonia or certain ammonia precursors, or aqueous solutions of either, into an oxygen-rich waste gas for selective reaction with the nitrogen monoxide at a temperature in the range of from  $870^\circ$  to  $1100^\circ\text{C}$ . While the lower temperature limit can be reduced by the addition of certain substances, it is important that the temperature of the combustion effluent lie within a narrow "temperature window" during the contact with the gaseous ammonia to achieve maximum utilization of the ammonia for reduction of  $\text{NO}$ . Inefficient utilization increases costs and causes other problems associated with ammonia discharge, such as reaction with the sulfur to form solid ammonium sulfate and/or bisulfite which deposit on heat exchange surfaces and can quickly reduce heat transfer efficiency.

Arand et al disclose in U.S. Patent 4,208,386 that urea can be added alone or in solution to oxygen-rich effluents in a temperature range from  $700^\circ$  to  $1100^\circ\text{C}$ . Similarly, in U.S. Patent 4,325,924, Arand et al describe an SNCR process utilizing urea in fuel-rich combustion effluents. Any urea

-5-

which fails to react with  $\text{NO}_x$  within the defined temperature windows is, nonetheless chemically transformed by heat and some, during cooling, results in ammonia formation.

A number of other patents define methods for operating at temperatures outside of the narrow ranges defined above for SNCR. For example, in U.S. Patent 4,992,249, Bowers discloses that if droplet size is increased and urea concentration is decreased, good results can be achieved in oxygen-rich effluents at higher temperatures than disclosed by Arand et al. And, in U.S. Patent 4,719,092, Bowers discloses that an additional material, an oxygen-containing hydrocarbon, can be introduced with the urea solution to reduce residual ammonia concentration in the effluent. Despite the ability of these processes to move the temperature window either higher or lower, the opening in the window remains fairly constant and distribution of the active chemicals at the operative temperature remains important. These patents do not recognize the difficulties in achieving suitable distribution where the temperature gradients across the plane of intended chemical introduction are too great.

Various nozzles and injectors have been designed to provide better distribution of chemicals into injection passages; however, without an understanding of the present invention, the achievement of satisfactory chemical distribution will remain an extremely difficult task. The recognition that operational factors such as entrained solids cause a predictable departure from conventionally understood temperature distributions, is essential to effective control of SNCR processes.

-6-

**Disclosure of Invention**

It is an object of the invention to improve the introduction and utilization of pollutant-reducing chemicals in effluents which are characterized by large temperature gradients in the direction transverse to flow, such as particulate-laden combustion effluents.

It is another object of the invention to improve the reliability of SNCR  $\text{NO}_x$ -reducing installations which depend on the introduction of aqueous solutions of  $\text{NO}_x$ -reducing agents into combustion effluents which contain large amounts of entrained solids.

It is another object to mitigate utilization and distribution problems associated with SNCR processes in coal-fired installations.

A yet further, but related, object is to mitigate utilization and distribution problems associated with SNCR processes in installations employing sorbent injection for  $\text{SO}_x$  reduction.

These and other objects are achieved by the present invention which provides an improved process for reducing the concentration of nitrogen oxides in a flowing stream of combustion effluent, comprising: determining the temperature at a plurality of points on a plane transverse to the flow of combustion effluent; based on the determined temperatures, defining a near-wall zone which has an average temperature effective for  $\text{NO}_x$  reduction by selective noncatalytic reduction utilizing a suitable  $\text{NO}_x$ -reducing composition, and a central zone having an average temperature above the effective  $\text{NO}_x$ -reducing temperature with that composition; and introducing  $\text{NO}_x$ -reducing composition into the effluent for reaction within the near-wall zone. The process has



-7-

particular application in the treatment of effluents laden with entrained particulate solids, such as those from coal- and other solid fuel-fired combustors and those which have been contacted with solid sorbents for  $\text{SO}_x$  reduction.

It is important to employ the process of the invention where the difference between the average temperatures of the two zones is greater than about  $100^\circ\text{C}$ , and especially where the temperature difference is  $200^\circ\text{C}$  or higher. At least a portion of the  $\text{NO}_x$ -reducing composition is introduced into the near-wall zone as fine droplets of an aqueous solution, preferably the droplets being of a size effective to assure evaporation of substantially all of the aqueous carrier within the near-wall zone.

In one preferred embodiment,  $\text{NO}_x$ -reducing composition is also introduced as medium-to-large diameter aqueous droplets with a size, momentum and concentration to pass into and through the central zone without significantly reacting until the temperature of the effluent in that zone is reduced to a level effective for  $\text{NO}_x$  reduction. The concentration of the water and active  $\text{NO}_x$ -reduction composition in the droplets which enter the central zone at high temperature, are selected for the droplet size range and injection velocity so that the water protects the active composition during high-temperature residence. The water should be sufficiently evaporated upon entering the lower temperatures downstream to quickly release the active  $\text{NO}_x$ -reducing composition within the effective temperature range. Introduction of small as well as large droplets can be achieved with a single or a multiplicity of injectors, as desired.

It is also preferred that the above process be employed as the first stage of a multi-stage process. Desirably, a second stage injection of the same or a different composition can be utilized to further reduce  $\text{NO}_x$  or other pollut-

-8-

ant. Third and subsequent stages can be employed as desired.

In another embodiment, an excess of  $\text{NO}_x$ -reducing composition can be effectively employed in the near-wall zone to maximize  $\text{NO}_x$ -reduction and produce ammonia slip. This is effective where ammonia by-product is mixed by convective currents with at least a portion of the central zone effluent after it has been cooled to an effective temperature for reaction.

#### Brief Description of the Drawings

The invention will be better understood and its advantages will become more apparent when the following detailed description is read in conjunction with the accompanying drawings, in which:

Figure 1 is a vertical cross section of a large scale combustor showing isotherms at a representative load condition and one arrangement of injectors for introducing active chemicals for reducing  $\text{NO}_x$  in accordance with the invention; and

Figure 2 is a three-dimensional view showing isotherms in a large scale combustor as surfaces and showing multiple level injection, with injectors at each level positioned at several locations around the combustor perimeter as would be necessary to provide good coverage of active chemical.

#### Best Mode for Carrying Out the Invention

Effluents in need of treatment are produced by a variety of sources including large industrial and utility boilers, incinerators, circulating fluidized bed boilers, and

-9-

the like. Some of these, like coal- and wood-fired boilers will naturally produce effluents with high solids loadings. Others, such as those burning oil with significant sulfur content, produce effluents with high  $\text{SO}_x$  contents which are treated by dry or wet injection of sorbents such as calcium carbonate, calcium bicarbonate, lime, or the like. It will be understood, however, that the invention is applicable in any high temperature environment where high temperature gradients, such as caused by the presence of entrained solids, interfere with the reduction of nitrogen oxides by selective gas-phase reaction.

Figure 1 depicts a vertical cross-section of a large-scale combustor 10 and shows isotherms determined within the effluent at a representative load condition. Burner 20 is shown to create a combustion flame 22 by burning a fuel such as coal with combustion air near the bottom of the combustion chamber 12. Hot combustion gases form an effluent which moves upwardly from the flame. For the purpose of definition, the term "effluent passage" is meant to include the entire structure through which the hot combustion gases flow, including the combustion chamber 12, vertical passage 14, horizontal passage 16, and subsequent structure (not shown).

As the effluent rises, zones of differential temperature develop due to a number of influences -- significant among which are the effect of heat exchange through effluent passage walls and particulate solids entrained within the hot gases. The entrained solids near the heat absorbing walls tend to radiate heat efficiently over short path lengths. Thermal radiation from the central portions of the gas is refracted or otherwise attenuated by the entrained solids. Figure 1 shows representative isotherms, e.g. at  $1300^\circ\text{C}$ ,  $1200^\circ\text{C}$ ,  $1050^\circ\text{C}$  and  $950^\circ\text{C}$ , illustrating temperature

-10-

gradients greater than 200° to 350°C and more at some horizontal cross sections where the measurable temperatures near the walls would be apparently ideal for SNCR, typically from 950° to 1050°C. Temperature gradients of these magnitudes make ineffective those SNCR procedures which attempt injection of uniformly-sized droplets to achieve uniform coverage across a plane transverse to the direction of flow.

It is typical in the case of effluents with high solids loadings (e.g., greater than 5 grams/normal cubic meter) that the difference between the average flue gas temperatures near the wall and near the center of the unit is at least about 100°C, typically at least 200°C, and can be 350°C or more higher. At least a portion of the NO<sub>x</sub>-reducing composition is preferably introduced into the near-wall zone at this location as fine droplets of an aqueous solution, to assure evaporation of substantially all of the aqueous carrier from these droplets within the near-wall zone. In most cases, a least some of the droplets should be larger and be injected at sufficient velocity to enter the central zone and survive until they pass through it.

The present invention calls for determining the temperature of the effluent at a sufficient number of locations that a temperature profile can be determined to define a near-wall zone where the temperature conditions favor SNCR reactions, and a central zone where the temperature is too high. This can be accomplished by means of a suction pyrometer employing a k-type thermocouple. It is also desired to determine effluent velocities at a sufficient number of locations to permit the use of a suitable computational fluid dynamics (CFD) modeling technique to establish a three-dimensional temperature profile, such as illustrated in Figure 2, to determine the best location within the near-wall zone for introducing the NO<sub>x</sub>-reducing composition. For applications with construction in the future or where direct

-11-

measurements are impractical, CFD modeling alone can sufficiently predict furnace conditions.

The injection locations into the near-wall zone, and the droplet velocity, size and concentration, are facilitated by computational fluid dynamics and chemical kinetic modeling (CKM) techniques. In reference to the CFD and CKM techniques, see the following publication and the references cited therein: Sun, Michels, Stamatakis, Comparato, and Hofmann, "Selective Non-Catalytic NO<sub>x</sub> Control with Urea: Theory and Practice, Progress Update", *American Flame Research Committee, 1992 Fall International Symposium, October 19-21, 1992, Cambridge, MA.*

Figure 1 shows one arrangement of injectors for introducing active chemicals for reducing NO<sub>x</sub> in accordance with the invention. Two levels of injection are shown, but the invention can be carried out with a single zone where conditions permit. Typically, however, it is preferred to employ multiple stages. This permits both the injection of different compositions simultaneously or the introduction of compositions at different locations or with different injectors to follow the temperature variations which follow changes in load. See in this regard, U.S. Patent 4,777,024 to Epperly et al. The location of injection and chemical formulation can be varied to meet the temperature and compositional variations in the gas stream being treated as described in U.S. Patent 4,780,289 to Epperly et al. Desirably, a second stage injection of the same or a different composition is employed to further reduce NO<sub>x</sub> or other pollutant. Third and subsequent stages can be employed as desired.

In Figure 1, a first level of introduction 30 is illustrated as providing sprays having a droplet size distribution which includes smaller droplets for shallow penetration

-12-

into the near-wall zone and larger droplets with deeper penetration into the central zone. For practical purposes with urea solutions, the near-wall zone is preferably from about 950° to 1050° C, and the central zone will include the higher temperatures, at this level. The other level of introduction illustrated as 130, is farther downstream and is shown as providing a spray which again penetrates only the near-wall zone at that location. The exact location of the sprays and their spray patterns can be determined for optimum results by computational fluid dynamics techniques -- given an appreciation of the distinct temperature zones which occur, such as in high solids environments and an understanding that the different horizontal cross-sectional temperature zones must be treated separately.

In most SNCR processes, the treatment composition is introduced into the effluent by an injector which generally comprises a conduit, sometimes fitted at the tip with a nozzle, extending into an effluent gas stream. In some cases a portion of effluent or other gas is employed to help atomize and disperse the treatment composition. The spray or injection pattern is defined with precision, often measured with the aid of computerized data acquisition to assure good distribution and reaction. Apparatus of varying degrees of sophistication are known. Some comprise coaxial, multi-tubular structures, such as those disclosed by Burton in U.S. Patent 4,842,834, by DeVita in U.S. Patent 4,985,218, and by Chawla et al in WO 91/17814, the disclosures of each of which are incorporated herein by reference. Injectors of these and other designs can be used to achieve the desired injection pattern, droplet sizes, droplet concentrations and droplet velocities to achieve the objectives of the invention.

Typically, in SNCR processes an attempt is made to penetrate the effluent stream with complete coverage in a

-13-

plane transverse to the direction of effluent flow. The present invention helps improve operation by defining a near-wall zone having suitable temperatures for SNCR and introducing active chemicals into that zone, despite the fact that hotter than desired temperatures exist on that same plane. The improvement is facilitated by introducing fine droplets to be utilized in the near-wall zone and large droplets which enter the central zone but survive until they reach a lower temperature zone downstream.

Referring again to Figure 2, a plurality of injectors 230 will typically be employed around the perimeter of the combustor. The injectors are preferably spaced one from the other as uniformly as is consistent with effectiveness which will vary with velocity and temperature profiles within the effluent passage. Typically, to achieve uniform coverage with fine droplets in the near-wall zone, nozzles will be spaced from about 1 to about 3 meters apart. While not shown, for clarity, it is also desired to inject larger droplets at at least the first stage. Introduction of small as well as large droplets can be achieved with a single or a multiplicity of injectors, as desired.

The coverage of the central zone, which is hotter than the near-wall zone, is accomplished by injecting the  $\text{NO}_x$ -reducing composition farther downstream (where the effluent has cooled) or by injecting larger droplets at relatively low concentration and high velocity so that they survive the higher temperatures and release the active agent farther downstream where the temperature is more suitable for SNCR. When operated optimally, chemical utilization is increased, undesired by-products are decreased, and the chances for impingement with and damaging of heat exchange and other equipment surfaces is greatly reduced.

-14-

Droplet sizes indicated below are determined with a Malvern 2600 instrument, utilizing a Fraunhofer diffraction, laser-based system. And, unless otherwise indicated, all parts and percentages are based on the weight of the composition at the particular point of reference.

It is preferred that at least a portion (e.g., at least 10%) of the  $\text{NO}_x$ -reducing composition be introduced into the near-wall zone in a form to have its intended effect therein. Preferably, it is dispersed from a nozzle to provide uniformly fine droplets, e.g. having an average droplet size within the range of from about 5 to about 100 microns Sauter mean diameter. The concentration of the active chemical and water in the fine droplets should permit complete release within this zone. Thus, relatively high concentrations of  $\text{NO}_x$ -reducing chemical, e.g. 20 to 50%, are preferred for this purpose. Droplet injection velocities are not particularly important if sizes are small enough, but can reasonably be in the range of from 5 to 60 m/sec.

It is also preferred that a portion of the  $\text{NO}_x$ -reducing composition which is introduced into the near-wall zone of suitable reaction temperature, be injected so as to pass through the near-wall zone and into the central zone. Because the central zone is too hot for good SNCR reaction, the droplets should be of a size, concentration and velocity effective to pass through the portion of the zone which is too hot, survive until lower temperatures prevail downstream and there release the active chemical. The concentration of the water and active  $\text{NO}_x$ -reducing composition in the droplets which enter the central zone at high temperature are selected so that the water protects the active composition during high-temperature residence. The water should be sufficiently evaporated upon entering the lower temperatures downstream to quickly release the active  $\text{NO}_x$ -reducing composition within the effective temperature range. For these purposes,



-15-

the droplets will preferably be of a size of from 100 to 1000, e.g. from 100 to 500 microns Sauter mean diameter, a concentration of from 2 to 35% active NO<sub>x</sub>-reducing agent, ideally of low volatility such as urea, and a velocity of from about 10 to 60 m/sec.

It is an advantage of the present invention that liquid droplets comprising NO<sub>x</sub>-reducing agents can be injected at well-controlled particle size distributions and velocities to make at least a portion of the active agent available near the point of injection in the near-wall zone while yet providing, as desired, droplets which will enter the central zone and survive desired temperature window for NO<sub>x</sub> reduction. This distribution of droplets can be accomplished using one or more injectors. Well-controlled polydispersity of droplet sizes will provide optimum results following the teachings of the invention.

The NO<sub>x</sub>-reducing agent is most desirably introduced as an aqueous treatment solution, such as urea or other NH-containing compositions, and can include one or more enhancers. The various treatment solutions are premixed to include the NO<sub>x</sub>-reducing composition and enhancer most appropriate for the range of temperatures expected to be encountered.

The total amount of the reducing agent injected into the effluent from all points should be sufficient to obtain a reduction of the nitrogen oxide concentration. In particular, the reducing agents are employed in total amounts sufficient to provide a molar ratio of reducing agent to baseline nitrogen oxide content (i.e., prior to treatment at that stage) of about 1:4 to about 5:1. The ratio is preferably within the range from 1:2 to 3:1, even more narrowly 2:3 to 2:1. In most situations this amount will be distributed jointly by a number of nozzles from a number of points as illustrated in Figure 1.

-16-

In one embodiment, an excess of  $\text{NO}_x$ -reducing composition can be effectively employed in the near-wall zone to maximize  $\text{NO}_x$  reduction and produce ammonia slip. This is effective where ammonia by-product is mixed by convective currents with at least a portion of the central zone effluent after it has been cooled to an effective temperature for reaction. Various  $\text{NH}$ -containing compositions, in their pure and typical commercial forms, will generate effective gas-phase agents (e.g., the amidogen radical) for SNCR when introduced in aqueous solution and subjected to elevated temperatures. Among the prominent  $\text{NH}$ -containing compositions are those selected from the group consisting of ammonia, urea, urea precursors, urea hydrolysis products, products of reaction of urea with itself or other compositions, related compositions, and mixtures of these. Among these compounds are ammonium carbonate, ammonium formate, ammonium citrate, ammonium acetate, ammonium oxalate, other ammonium salts (inorganic and organic) particularly of organic acids, ammonium hydroxide, various stable amines, guanidine, guanidine carbonate, biguanide, guanylurea sulfate, melamine, dicyanimide, calcium cyanamide, biuret, 1,1-azobisformamide, methylol urea, methylol urea-urea, dimethyl urea, hexamethylenetetramine (HMTA), and mixtures of these.

Among the hydrolysis products are ammonia, carbamates such as ammonium carbamate, ammonium carbonate, ammonium bicarbonate and other ammonia salts, various urea complexes and half ammonia salts. The exact form of some of these compounds is not known because the techniques employed to analyze them can affect their makeup. U.S. Patent 4,997,631 to Hofmann et al and PCT application WO 92/02291 to von Harpe et al, are incorporated herein by reference.

Enhancers are additive materials which modify the effectiveness of a pollutant-reducing agent in terms of its effective temperature window, its utilization efficiency, or

-17-

the like. Among the enhancers are the above materials when used in suitable combination, oxygenated hydrocarbons, and mixtures of these. Exemplary of the oxygenated hydrocarbons are ketones, aldehydes, alcohols including polyols, carboxylic acids, sugars, starch hydrolysates, hydrogenated starch hydrolysates, sugar-containing residues such as molasses, and mixtures of any of these. The entire disclosures of U.S. Patents 4,719,092, 4,844,878 and 4,877,591 are incorporated herein by reference.

It is an option to incorporate in the solutions of the invention, a hardness-suppressing composition comprising at least one member selected from the group consisting of polymers, phosphonates, chelants, phosphates and mixtures of any two or more of these, in an amount effective to suppress hardness. Thus, single members of this group can be employed where effective, or two or more members of a single group can be employed, as well as mixtures of members from different groups. Surfactants and stabilizers are also employed. The disclosure of Dubin et al U.S. Patent Application No. 07/770,857, filed October 3, 1991, is incorporated herein by reference.

Control of liquid droplet sizes can be facilitated by chemical as well as mechanical means. For example, the addition of surfactants can help provide smaller average droplet sizes as disclosed in U.S. Patent Application Serial No. 07/959,706 filed October 13, 1992 by D. Diep and L. Lin. Also, the addition of certain polymers can help provide larger droplet sizes as disclosed in U.S. patent Application Serial No. 07/959,705 filed October 13, 1992 by D. Diep, L. Lin and P. Christiansen. The various injectors and nozzles can be tested at various flow rates and pressures to determine their effect on droplet sizes.

-18-

The NO<sub>x</sub>-reducing compositions will typically be prepared and shipped as a concentrate which is diluted for use. Typically, these concentrates will contain 25 to 65% urea, and 0.05 to 1.0 % of an effective hardness-suppressing composition. The urea and a separate additive package can be preblended to form this concentrate. This concentrate is typically diluted prior to injection as required to achieve a urea concentration effective under the injection conditions. Typically, dilution to concentrations of from 1 to 35% urea are effective. Typically, the pH of the aqueous solution is above 5, and generally is within the range of from 7 to 11, e.g., 8 to 10.

The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the invention. It is not intended to detail all of those obvious modifications and variations which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such obvious modifications and variations be included within the scope of the invention which is defined by the following claims. The claims are meant to cover the claimed components and steps in any sequence which is effective to meet the objectives there intended, unless the context specifically indicates the contrary.

-19-

## CLAIMS

1. A process for reducing the concentration of nitrogen oxides in a flowing stream of combustion effluent, comprising:

determining the temperature at a plurality of points on a plane transverse to the flow of combustion effluent;

based on the determined temperatures, defining a near-wall zone which has an average temperature effective for NO<sub>x</sub> reduction by selective noncatalytic reduction utilizing a suitable NO<sub>x</sub>-reducing composition, and a central zone which has an average temperature higher than suitable for NO<sub>x</sub> reduction with that composition; and

introducing NO<sub>x</sub>-reducing composition into the effluent within the near-wall zone.

2. A process according to claim 1 wherein the average temperature in the near-wall zone is at least 200°C lower than the average temperature in the central zone.

3. A process according to claim 1 wherein the average temperature in the near-wall zone is at least 350°C lower than the average temperature in the central zone.

4. A process according to claim 1 wherein the effluent is laden with entrained particulate solids.

5. A process according to claim 4 wherein the effluent is from a coal-fired or other solid fuel-fired combustor.

6. A process according to claim 4 wherein the effluent includes entrained solid sorbents introduced for SO<sub>x</sub> reduction.

7. A process according to claim 1 wherein at least a portion of the NO<sub>x</sub>-reducing composition is introduced into the

-20-

near-wall zone as fine droplets of an aqueous solution, the droplets being of a size effective and concentration to assure evaporation of substantially all of the water within the near-wall zone.

8. A process according to claim 7 wherein at least a portion of the  $\text{NO}_x$ -reducing composition is introduced as medium to large diameter aqueous droplets with a size, momentum and concentration effective to cause the droplets to pass into and through the central zone without significantly reacting until the temperature of the effluent in that zone is reduced to a range effective for  $\text{NO}_x$  reduction.
9. A process according to claim 8 wherein the introduction of fine and large droplets is accomplished by the same injector.
10. A process according to claim 8 wherein a multiplicity of injectors is employed to introduce large and fine droplets.
11. A process according to claim 1 wherein  $\text{NO}_x$ -reducing composition comprises an NH-containing composition.
12. A process according to claim 11 wherein the  $\text{NO}_x$ -reducing composition comprises an aqueous solution of a member selected from the group consisting of ammonia, urea, urea precursors, urea hydrolysis products, carbamates, ammonium carbonate, ammonium bicarbonate, cyanurates, ammonium salts of organic acids, other amidozine-generating compositions and mixtures of these.
13. A process according to claim 12 wherein the  $\text{NO}_x$ -reducing agent comprises urea or at least one of its hydrolysis products or a salt thereof.

-21-

14. A process for reducing the concentration of nitrogen oxides in a flowing stream of combustion effluent laden with entrained particulates at a level of at least 5 g/Nm<sup>3</sup>, comprising:

determining the temperature at a plurality of points on a plane transverse to the flow of combustion effluent;

based on the determined temperatures, defining a near-wall zone which has an average temperature effective for NO<sub>x</sub> reduction by selective noncatalytic reduction utilizing a suitable NO<sub>x</sub>-reducing composition, and a central zone which has an average temperature at least 300°C higher than that of the near-wall zone; and

introducing NO<sub>x</sub>-reducing composition into the effluent, at least a portion being injected into the near-wall zone as fine droplets,

wherein said NO<sub>x</sub>-reducing composition comprises an aqueous solution of a member selected from the group consisting of ammonia, urea, urea precursors, urea hydrolysis products, carbamates, ammonium carbonate, ammonium bicarbonate, cyanurates, ammonium salts of organic acids, other amidozine-generating compositions and mixtures of these, and

said fine droplets being of from 5 to 100 microns Sauter mean diameter.

15. A process according to claim 14 wherein at least a portion of the NO<sub>x</sub>-reducing composition is introduced as medium to large diameter aqueous droplets with a size, momentum and concentration effective to cause the droplets to pass into and through the central zone without significantly reacting until the temperature of the effluent in that zone is reduced to a range effective for NO<sub>x</sub> reduction.

16. A process according to claim 14 wherein the effluent is from a coal-fired or other solid fuel-fired combustor.

-22-

17. A process according to claim 14 wherein the effluent includes entrained solid sorbents introduced for SO<sub>x</sub> reduction.

18. A process for reducing the concentration of nitrogen oxides in a flowing stream of combustion effluent laden with entrained particulates at a level of at least 5 g/m<sup>3</sup>, comprising:

determining the temperature at a plurality of points on a plane transverse to the flow of combustion effluent;

based on the determined temperatures, defining a near-wall zone which has an average temperature effective for NO<sub>x</sub> reduction by selective noncatalytic reduction utilizing a suitable NO<sub>x</sub>-reducing composition, and a central zone which has an average temperature at least 300°C higher than that of the near-wall zone; and

introducing NO<sub>x</sub>-reducing composition comprising an aqueous solution of an active component which is a member selected from the group consisting of ammonia, urea, urea precursors, urea hydrolysis products, carbamates, ammonium salts of organic acids, other amidozine-generating compositions and mixtures of these;

at least a portion of said composition being introduced into said near-wall zone in droplets of a size of from 5 to 100 microns Sauter mean diameter and at a concentration of from 50 to 98% water, and at least a portion of the NO<sub>x</sub>-reducing composition is introduced as medium to large diameter aqueous droplets with a size of from 100 to 1000 microns, and momentum and concentration effective to cause the droplets to pass into and through the central zone without significantly reacting until the temperature of the effluent in that zone is reduced to a range effective for NO<sub>x</sub> reduction, said concentration of the active NO<sub>x</sub>-reduction composition in the droplets enter and which pass through the central zone at high temperature is selected so that the water in the droplets protects the active component during



-23-

high-temperature residence in the central zone and is sufficiently evaporated upon entering the lower temperatures downstream to quickly release the active NO<sub>x</sub>-reducing composition within the effective temperature range.

19. A process according to claim 17 wherein the average temperature in the near-wall zone is at least 350°C lower than the average temperature in the central zone.

20. A process according to claim 17 wherein the effluent is from a coal-fired or other solid fuel-fired combustor.

## AMENDED CLAIMS

[received by the International Bureau on 03 October 1994 (03.10.94); original claims 1 and 8-10 amended; original claims 2,4 and 7 cancelled; all claims renumbered 1-17 (5 pages)]

1. A process for reducing the concentration of nitrogen oxides in a flowing stream of combustion effluent laden with entrained particulate solids which cause large temperature gradients transverse to the direction of effluent flow, comprising:
  - determining the temperature at a plurality of points on a plane transverse to the flow of combustion effluent;
  - based on the determined temperatures, defining a near-wall zone which has an average temperature effective for NO<sub>x</sub> reduction by selective noncatalytic reduction utilizing a suitable NO<sub>x</sub>-reducing composition, and a central zone which has an average temperature higher than suitable for NO<sub>x</sub> reduction with that composition, the average temperature in the near-wall zone being at least 200°C lower than the average temperature in the central zone; and
  - introducing NO<sub>x</sub>-reducing composition into the effluent within the near-wall zone as fine droplets of an aqueous solution, the droplets being of a size of from 5 to 100 microns Sauter mean diameter which is effective and concentration which assures evaporation of substantially all of the water within the near-wall zone.
2. A process according to claim 1 wherein the average temperature in the near-wall zone is at least 350°C lower than the average temperature in the central zone.
3. A process according to claim 2 wherein the effluent is from a coal-fired or other solid fuel-fired combustor.

4. A process according to claim 2 wherein the effluent includes entrained solid sorbents introduced for SO<sub>x</sub> reduction.
5. A process according to claim 2 wherein at least a portion of the NO<sub>x</sub>-reducing composition is introduced as aqueous droplets larger than said fine droplets with a size of at least 100 microns Sauter mean diameter, and momentum and concentration effective to cause the droplets to pass into and through the central zone without significantly reacting until the temperature of the effluent in that zone is reduced to a range effective for NO<sub>x</sub> reduction.
6. A process according to claim 5 wherein the introduction of fine and the larger droplets is accomplished by the same injector.
7. A process according to claim 5 wherein a multiplicity of injectors is employed to introduce large and the fine and the larger droplets.
8. A process according to claim 1 wherein NO<sub>x</sub>-reducing composition comprises an NH-containing composition.
9. A process according to claim 8 wherein the NO<sub>x</sub>-reducing composition comprises an aqueous solution of a member selected from the group consisting of ammonia, urea, urea precursors, urea hydrolysis products, carbamates, ammonium carbonate, ammonium bicarbonate, cyanurates, ammonium salts of organic acids, other amidozine-generating compositions and mixtures of these.
10. A process according to claim 9 wherein the NO<sub>x</sub>-reducing agent comprises urea or at least one of its hydrolysis products or a salt thereof.

11. A process for reducing the concentration of nitrogen oxides in a flowing stream of combustion effluent laden with entrained particulates at a level of at least  $5 \text{ g/Nm}^3$ , comprising:

determining the temperature at a plurality of points on a plane transverse to the flow of combustion effluent;

based on the determined temperatures, defining a near-wall zone which has an average temperature effective for  $\text{NO}_x$  reduction by selective noncatalytic reduction utilizing a suitable  $\text{NO}_x$ -reducing composition, and a central zone which has an average temperature at least  $300^\circ\text{C}$  higher than that of the near-wall zone; and

introducing  $\text{NO}_x$ -reducing composition into the effluent, at least a portion being injected into the near-wall zone as fine droplets,

wherein said  $\text{NO}_x$ -reducing composition comprises an aqueous solution of a member selected from the group consisting of ammonia, urea, urea precursors, urea hydrolysis products, carbamates, ammonium carbonate, ammonium bicarbonate, cyanurates, ammonium salts of organic acids, other amidozine-generating compositions and mixtures of these, and

said fine droplets being of from 5 to 100 microns Sauter mean diameter.

12. A process according to claim 11 wherein at least a portion of the  $\text{NO}_x$ -reducing composition is introduced as medium to large diameter aqueous droplets with a size, momentum and concentration effective to cause the droplets to pass into and through the central zone without significantly reacting

until the temperature of the effluent in that zone is reduced to a range effective for NO<sub>x</sub> reduction.

13. A process according to claim 11 wherein the effluent is from a coal-fired or other solid fuel-fired combustor.

14. A process according to claim 11 wherein the effluent includes entrained solid sorbents introduced for SO<sub>x</sub> reduction.

15. A process for reducing the concentration of nitrogen oxides in a flowing stream of combustion effluent laden with entrained particulates at a level of at least 5 g/m<sup>3</sup>, comprising:

determining the temperature at a plurality of points on a plane transverse to the flow of combustion effluent;

based on the determined temperatures, defining a near-wall zone which has an average temperature effective for NO<sub>x</sub> reduction by selective noncatalytic reduction utilizing a suitable NO<sub>x</sub>-reducing composition, and a central zone which has an average temperature at least 300°C higher than that of the near-wall zone; and

introducing NO<sub>x</sub>-reducing composition comprising an aqueous solution of an active component which is a member selected from the group consisting of ammonia, urea, urea precursors, urea hydrolysis products, carbamates, ammonium salts of organic acids, other amidozine-generating compositions and mixtures of these;

at least a portion of said composition being introduced into said near-wall zone in droplets of a size of from 5 to 100 microns Sauter mean diameter and at a concentration of from 50 to 98% water, and at least a portion of the NO<sub>x</sub>-reducing composition is introduced as medium to large diameter aqueous droplets with a size of from 100 to 1000 microns, and momentum and concentration effective to cause the

droplets to pass into and through the central zone without significantly reacting until the temperature of the effluent in that zone is reduced to a range effective for NO<sub>x</sub> reduction, said concentration of the active NO<sub>x</sub>-reduction composition in the droplets enter and which pass through the central zone at high temperature is selected so that the water in the droplets protects the active component during high-temperature residence in the central zone and is sufficiently evaporated upon entering the lower temperatures downstream to quickly release the active NO<sub>x</sub>-reducing composition within the effective temperature range.

16. A process according to claim 14 wherein the average temperature in the near-wall zone is at least 350°C lower than the average temperature in the central zone.

17. A process according to claim 14 wherein the effluent is from a coal-fired or other solid fuel-fired combustor.

## STATEMENT UNDER ARTICLE 19

Claims 1 and 8-10 have been amended. Claims 2, 4, and 7, have been cancelled and the remaining claims have been renumbered.

All of the claims are now drawn to the solution to a problem which the art failed to recognize -- the effective treatment of a cross sectional area of a furnace wherein temperatures near the wall are suitable for SNCR, but those in the center are not. Applicants believe that the state of the art was not sufficiently developed to deal with this specifically-claimed situation. The technical problem was not addressed by the art.

Applicants urge, however, that the noted passages of the cited references do not explain that there are going to be some situations that the near-wall temperature is so radically different than the central portion, that small droplets must be introduced at the wall and large droplets can be introduced to reach the center.

Ruegg does not address the problem of finding and treating low temperature near wall effluent at a transverse plane where the central gas is greatly hotter. The reference to the second cited passage seems to indicate that choice of spray points is all that is necessary -- not recognizing that spray point is only one factor. The first cited passage again does not come to grips with the problem and indicates that temperatures are not that critical.

This is just the problem with the art before applicants' invention -- there was not a sufficient recognition of when, where, and to what extent the great temperature extremes occurred, especially in the context of high solids loading situations. If care is not taken -- and the art does not teach either the importance of vigilance of cross-sectional temperature variations, or to detect them and deal with them once detected -- some urea will be converted to ammonia which will slip through and some will be oxidized to actually create  $\text{NO}_x$ .

The claimed invention herein specifically addresses identifying nonuniformities and applying a specific combination of nonuniform treatment. Neither Bowers nor Ruegg address these concerns. There is no teaching to the art that high solids loading situations create large transverse temperature gradients but that a unique introduction of droplets of different sizes and of suitable concentrations and velocities can achieve SNCR even though it would appear otherwise to the skilled worker.

The claims as now amended are limited to this very unique problem and the solution found by applicants.



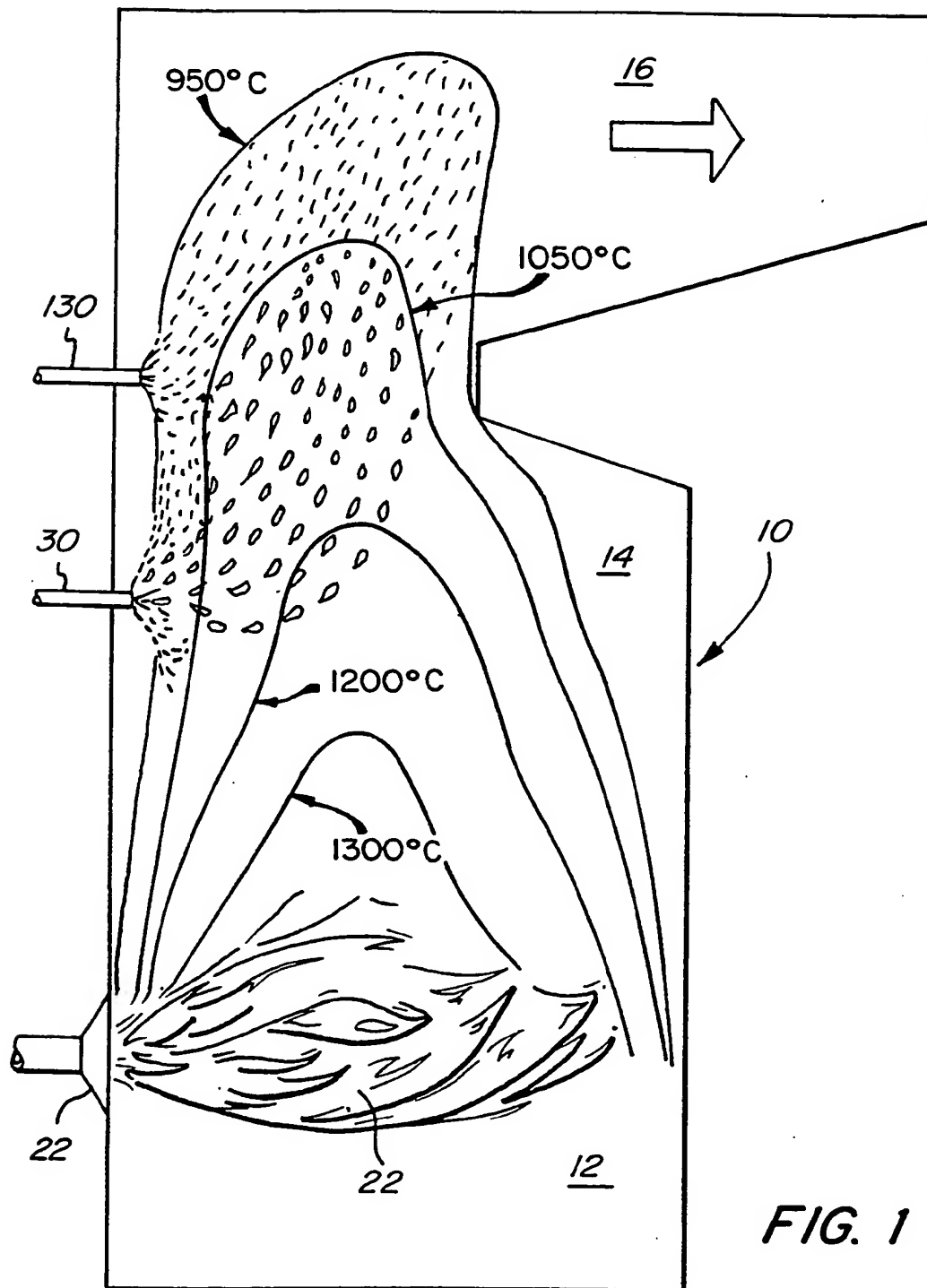


FIG. 1

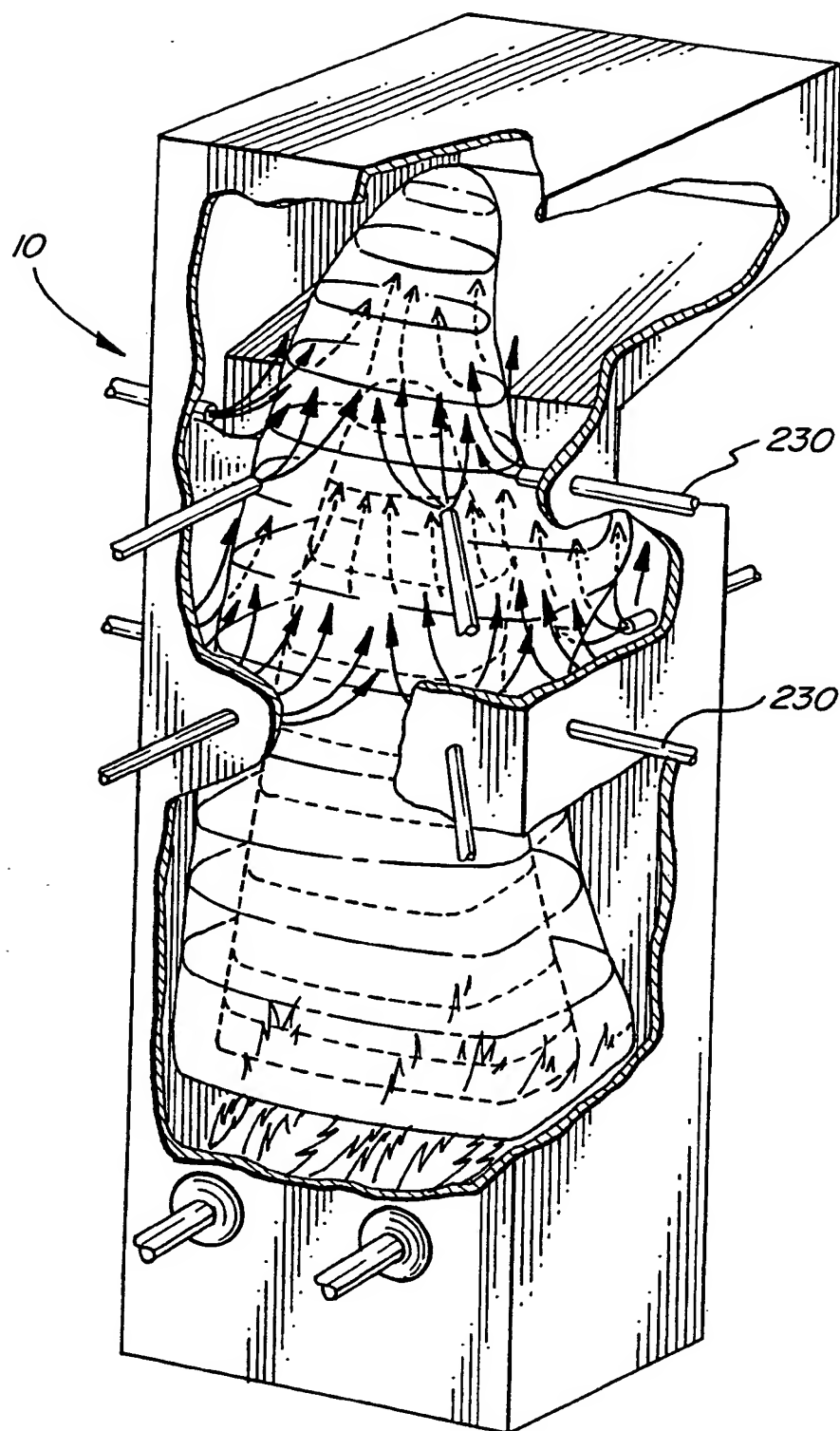


FIG. 2

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/05117

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C01B 21/20,  
US CL : 423/235, 239.1

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/235, 239.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

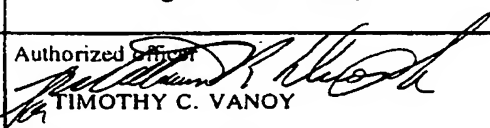
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,719,092 (BOWERS) 12 JANUARY 1988, SEE COL. 4 LINES 11-30.	1, 14, 18
Y	US, A, 5,045,292 (RÜEGG ET AL.) 03 SEPTEMBER 1991, SEE COL. 2 LINES 46-55, COL. 3 LINES 14-30, COL. 4, LINES 11-30 AND COL. 5 LINE 13 TO COL. 6 LINE 3.	1-20
A	US, A, 3,900,554 (LYON) 19 AUGUST 1975, SEE COL. 9 LINE 35 TO COL. 12 LINE 44.	1-20
A	US, A, 4,208,386 (ARAND ET AL.) 17 JUNE 1980, SEE COL. 5 LINE 5 TO COL. 6 LINE 18.	1-20
A	US, A, 4,325,924 (ARAND ET AL.) 20 APRIL 1982, SEE COL. 4 LINES 8-35.	1-20

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 05 JULY 1994	Date of mailing of the international search report 01 AUG 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer  TIMOTHY C. VANOY Telephone No. (703) 308-2540

Form PCT/ISA/210 (second sheet)(July 1992)\*

# INTERNATIONAL SEARCH REPORT

Int. .onal application No.  
PCT/US94/05117

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,777,024 (EPPERLY ET AL.) 11 OCTOBER 1988, SEE COL. 12 LINE 39 TO COL. 16 LINE 28.	1-20
A	US, A, 4,780,289 (EPPERLY ET AL.) 25 OCTOBER 1988, SEE COL. 16 LINE 65 TO COL. 19 LINE 64.	1-20
A	US, A, 4,844,878 (EPPERLY ET AL.) 04 JULY 1989, SEE COL. 14 LINE 63 TO COL. 16 LINE 64.	1-20
A	US, A, 4,877,591 (EPPERLY ET AL.) 31 OCTOBER 1989, SEE COL. 6 LINE 24 TO LINE 67.	1-20
A	US, A, 4,985,218 (DeVITA) 15 JANUARY 1991, SEE COL. 9 LINE 9 TO COL. 10 LINE 66.	1-20
A	US, A, 4,992,249 (BOWERS) 12 FEBRUARY 1991, SEE COL. 6 LINE 4 TO COL. 8 LINE 8.	1-20
A	US, A, 4,997,631 (HOFMANN ET. AL.) 05 MARCH 1991, SEE COL. 9 LINE 49 TO COL. 10 LINE 67.	1-20

Form PCT/ISA/210 (continuation of second sheet)(July 1992)\*